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DEGRADATION OF CHLOROETHENES IN AQUEOUS SOLUTION BY ULTRASOUND

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11th Meeting of the European Society of Sonochemistry, June 1-5 , La Grande Motte, France

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS AN OVERVIEW

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Chlorinated organocompounds are usually used as industrial solvents: CCl_4, $CHCl_3$, C_2Cl_4, C_2HCl_3 , among others, withspread environmental pollutants in the subsurface aquatic environment

harmful to human health and environment

which are difficult to treat by traditional technologies

- Air stripping
- Incineration
- Biodegradation
- Oxidation with chemicals
- Carbon adsorption

Development of new technologies

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS AN OVERVIEW

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- Development of new technologies (Advanced Oxidation Processes AOPs)
  Production of hydroxyl radical ($OH^{\cdot}$) as a primary oxidant:

  -Photochemical treatment (UV, UV/H_2O_2)
  -Ozonolysis
  -Fenton reaction $Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^{\cdot}$

- Application of ultrasound field is a successful tecnology for environmental clean-up

- Range of frequencies used 20-1000 kHz

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Ultrasound field

Cavitation (highT,P)

Physical effects (solution agitation)

Chemical effects (solvent sonolysis)

Pyrolytic degradation

Radicals generation → Pollutants oxidation

$$H_2O \xrightarrow{)))))} H^{\bullet} + OH^{\bullet}$$

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$$

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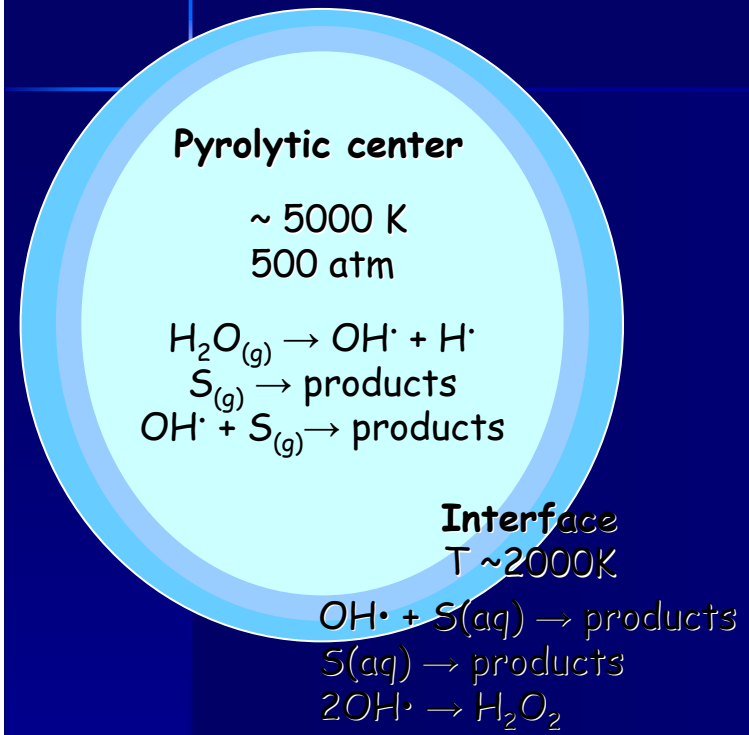

- During the cavitational collapse of single, isolated bubbles, extreme temperatures and pressures are achieved.
- The main chemical pathways for organic compound degradation include:
  - Hydroxyl chemical oxidation
  - Direct pyrolytic degradation
  - Supercritical water reactions: Water vapor splits during bubble cavitation to yield $H^{\cdot}$ and $OH^{\cdot}$
- Several organic compounds have been degradated using an ultrasonic field:
  - Aromatic compounds (phenol, chlorophenols)
  - Organic dyes
  - Herbicides and pesticides
  - Aliphatic carboxilic acids
  - Surfactants

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS
OBJECTIVES

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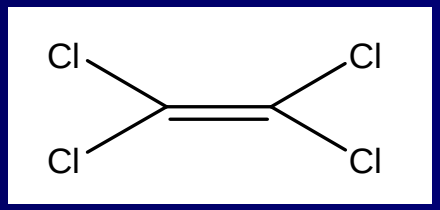
Study of the degradation of chlorinated organic compounds in aqueous solution using a 20 and 850 kHz ultrasound field



Degradation of perchloroethylene as a model molecule in aqueous solution

Abbreviation	Chemical name	Comercial name	Empirical formula
PCE	Tetrachloroethylene	perchloroethylene, perc, Ethylene tetrachloride, tetrachloroethene,	$CCl_2{=}CCl_2$

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RESULTS

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Property	
Molecular weight	165.83 g/mol
Melting point	-19ºC
Boiling point	121ºC
Density at 20ºC	1.6227g/mL
Solubility: Water at 25ºC	 150mg/L
Partition coefficients: Log K_{ow} Log K_{oc}	 3.40 2.2-2.7
Vapour pressure at 25ºC	18.47mm Hg
Henry´s law constant at 25ºC	1.8 x 10^{-2} atm m^3/mol

Properties perchloroethylene

Excellent solvent

↓

Applications
- -Dry-cleaning industry
- -Metal cleaning
- -Vapor degreasing

↓

Hazardous toxic compound

↓

US EPA Persistent pollutant

Table of physical and chemical properties of perchloroethylene

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS EXPERIMENTAL PROCEDURE

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- Perchloroethylene (Aldrich 99%) used as received.

-Solutions were prepared with purified water obtained from a Milli-Q system, 18.2 MΩ cm and previously deoxygenated by bubbling argon before addition of pechloroethylene.

- The solution was left stirring overnight.

-Temperature was kept at 20 ±1 ºC with a refrigerated bath and circulator.

-Ultrasonic irradiation was carried out at maximum volume (minimum headspace in the sonochemical reactor).

-Samples were analyzed inmediately after collection

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS RESULTS

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The degradation of perchloroethylene was studied by:

Analysis of aqueous phase

A) Following the chloride concentration formation in solution by Ion Exchange Chromatography

B) Monitoring of PCE and byproducts by High Performance Liquid Chromatograph (HPLC)

C) Detection and quantification of PCE and products from the degradation obtained at the end of each experiment was carried out using Purge and Trap Gas Chromatography Mass Spectrometry (PT-GC-MS)

Analysis of gaseous phase

A) Analysis CO/CO_2 by Gas Cromatographic with TCD (GC-TCD)
B) Anaysis of PCE and intermediates by Gas Cromatographic with FID (GC-FID)

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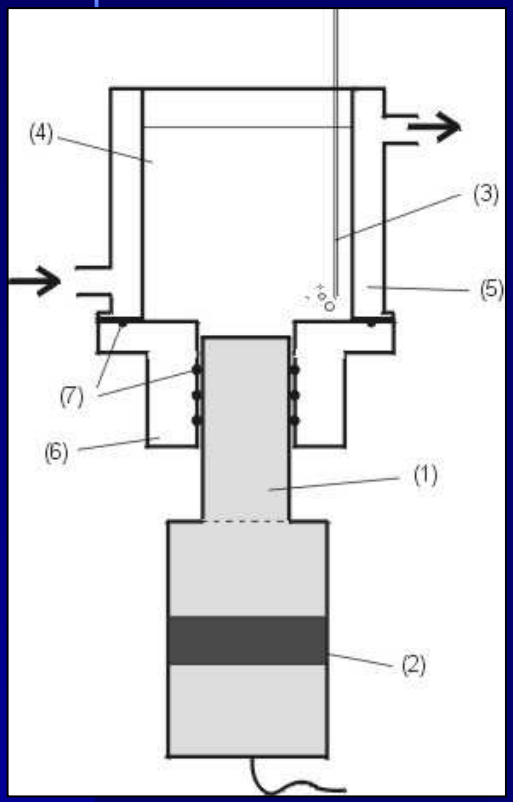
Experimental set-up



Sonoreactor (Undatim)
Frequency: 20kHz
Maximum power output: 100W

Hastelloy ultrasound horn: 3 cm diam.

Cell dimensions: diameter 68mm
depth 84mm

Sonicated volume: 200cm^3

(1) ultrasonic probe (2) transducer (3) gas passing (4) electrolyte (5) cooling jacket (6) Teflon adaptor (7) O-ring joints.

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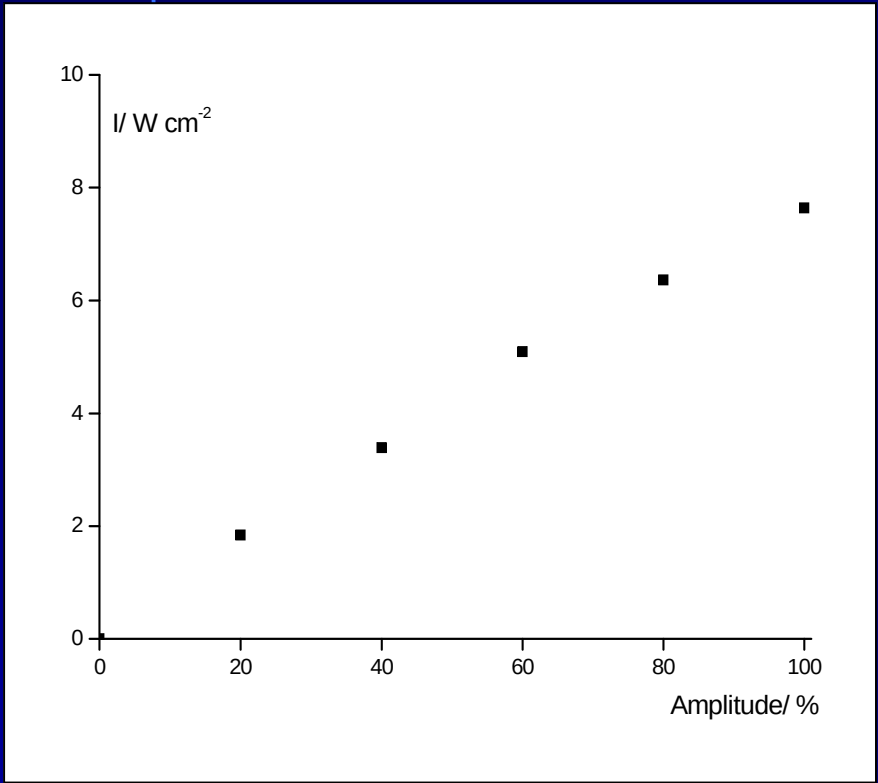
Characterization of the sonoreactor, 20kHz, 100W



Ultrasonic power input was measured using standard calorimetric procedures

Probe amplitude	Power dissipation in solution/ W	Acoustic intensity/ W cm^{-2}	Power density/ W mL^{-l}
20%	13	1.84	0.065
40%	24	3.39	0.120
60%	36	5.09	0.180
80%	45	6.36	0.225
100%	54	7.64	0.270

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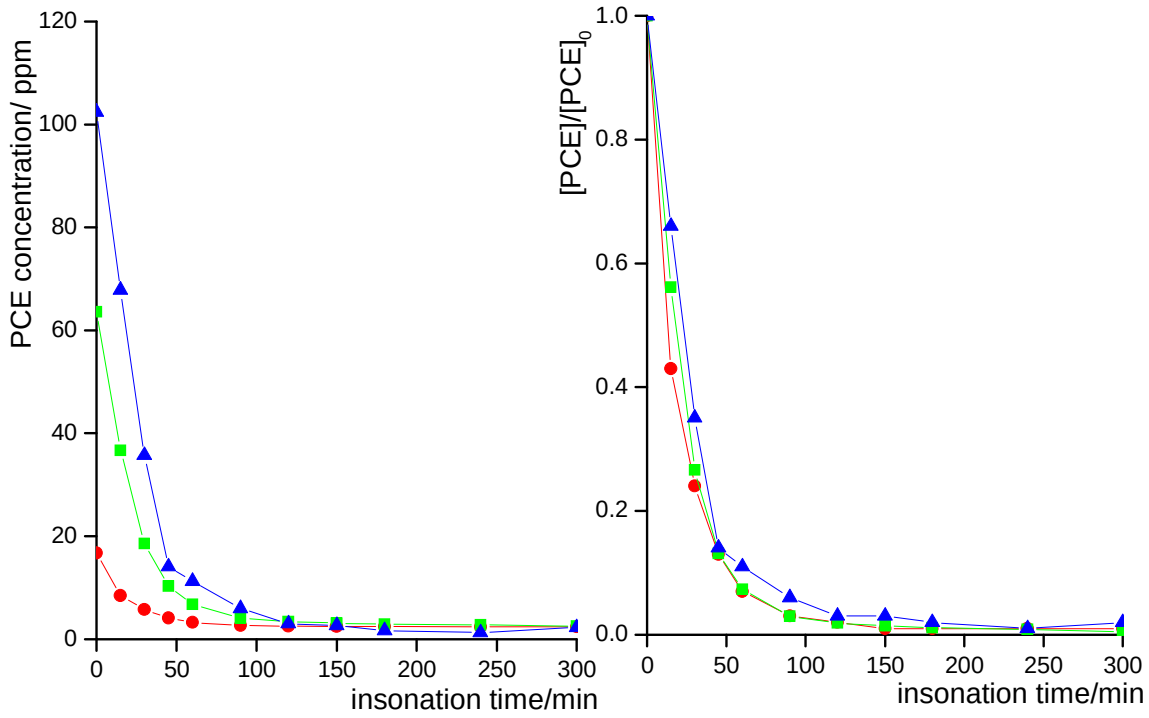
Initial concentration of PCE



Concentration decay is uneffected by initial concentration of PCE

- ● $[PCE]_0$ = 14ppm
- ■ $[PCE]_0$ = 64ppm
- ▲ $[PCE]_0$ = 100ppm

6.4 W cm^{-2}
5h
20kHz
20ºC

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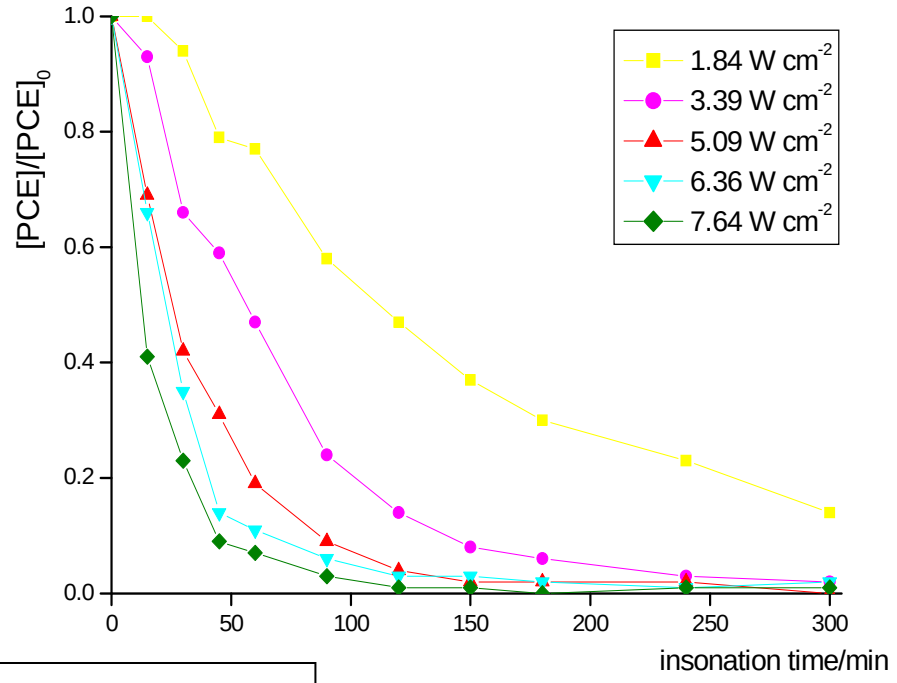
Ultrasonic intensity



$[PCE]_0 \approx 75ppm$
20kHz
5h
20ºC

The pH was found to decrease in all cases due to the HCl formation

I/ W cm^{-2}	Yield of chloride formation/ %
1.84	24
3.39	29
5.09	30
6.36	25
7.64	21

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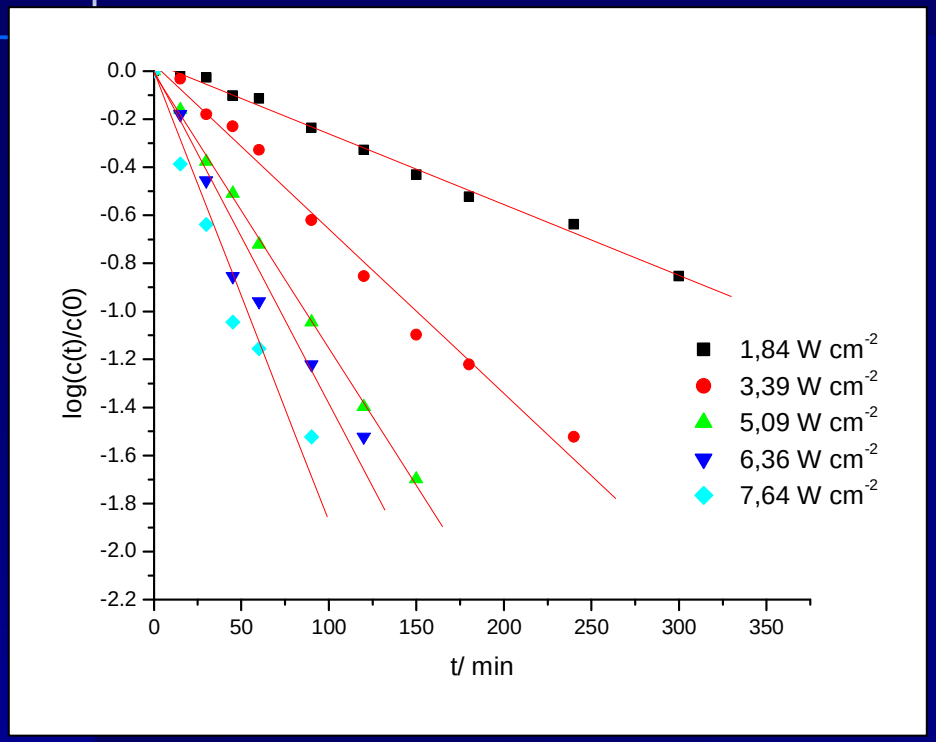
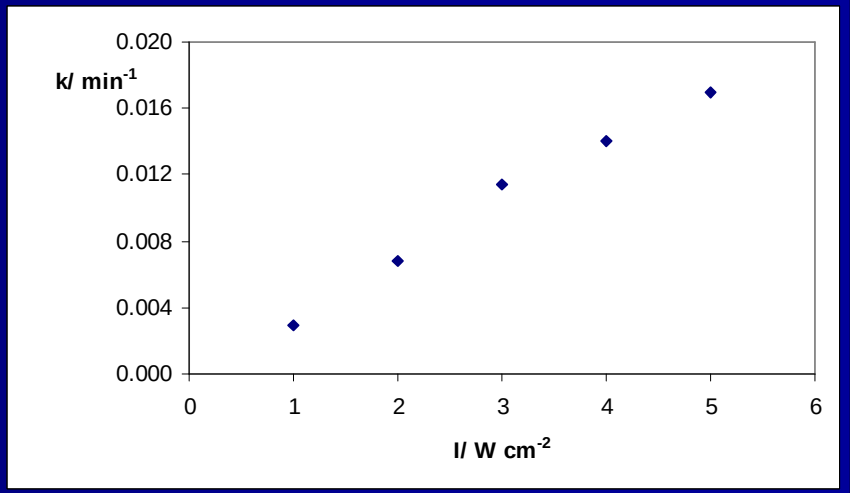
Ultrasonic intensity





Experimental results show that sonochemical destruction of PCE follows pseudo first-order kinetics

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS RESULTS

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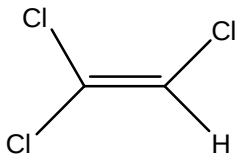
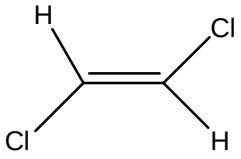
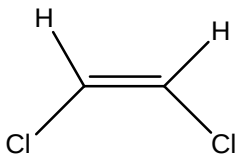
Main products from perchloroethylene sonochemical degradation:

TCE	Trans-DCE	cis-DCE
		
C_2Cl_3H	trans-$C_2Cl_2H_2$	cis-$C_2Cl_2H_2$

Products detected by P&T-GC-MS after 5h:

- $CHCl_3$
- CCl_4
- Hexachloroethane
- Hexachlorobutadiene
- Hexachloropropene

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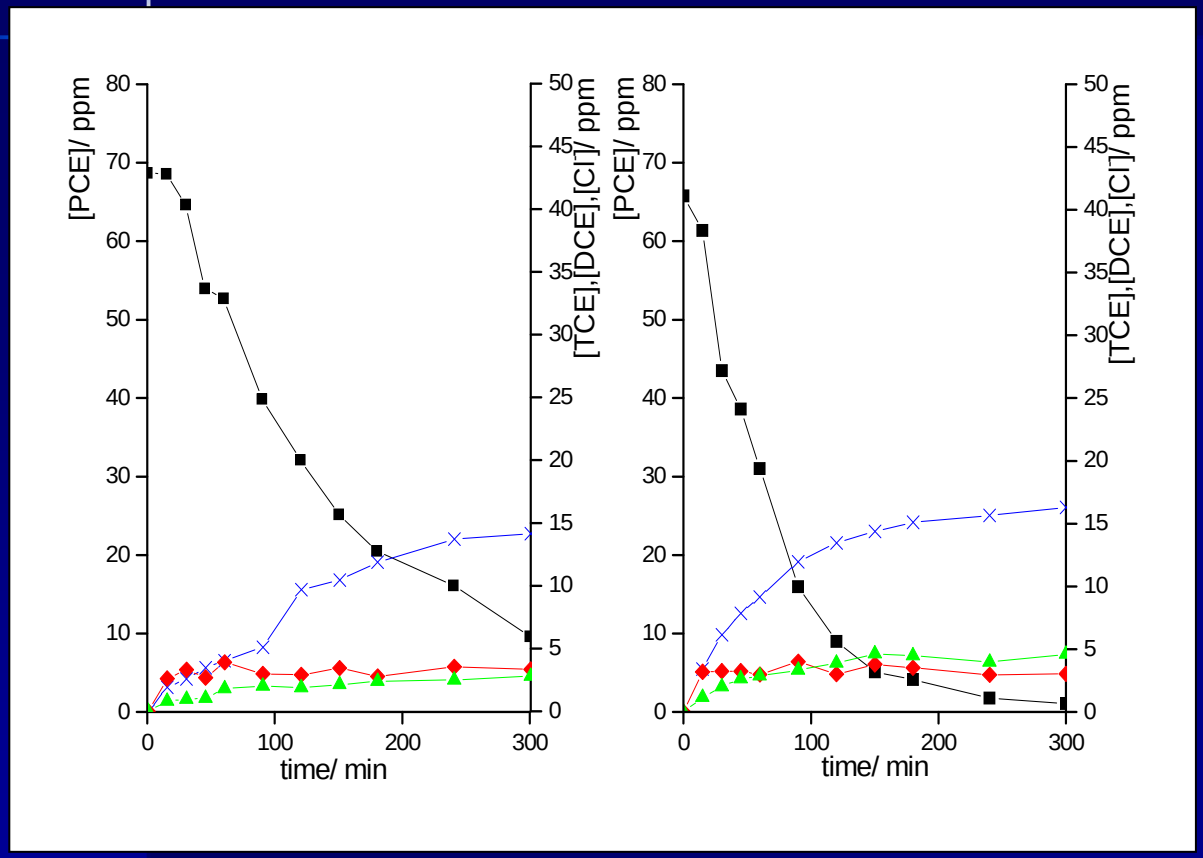
Ultrasonic intensity



Sonochemical treatment leads to TCE and DCE and chloride anions as major by-products

-■- [PCE]
-■- [TCE]
-▲- [DCE]
-×- [Cl^-]

1.84 W cm^{-2}

3.39 W cm^{-2}

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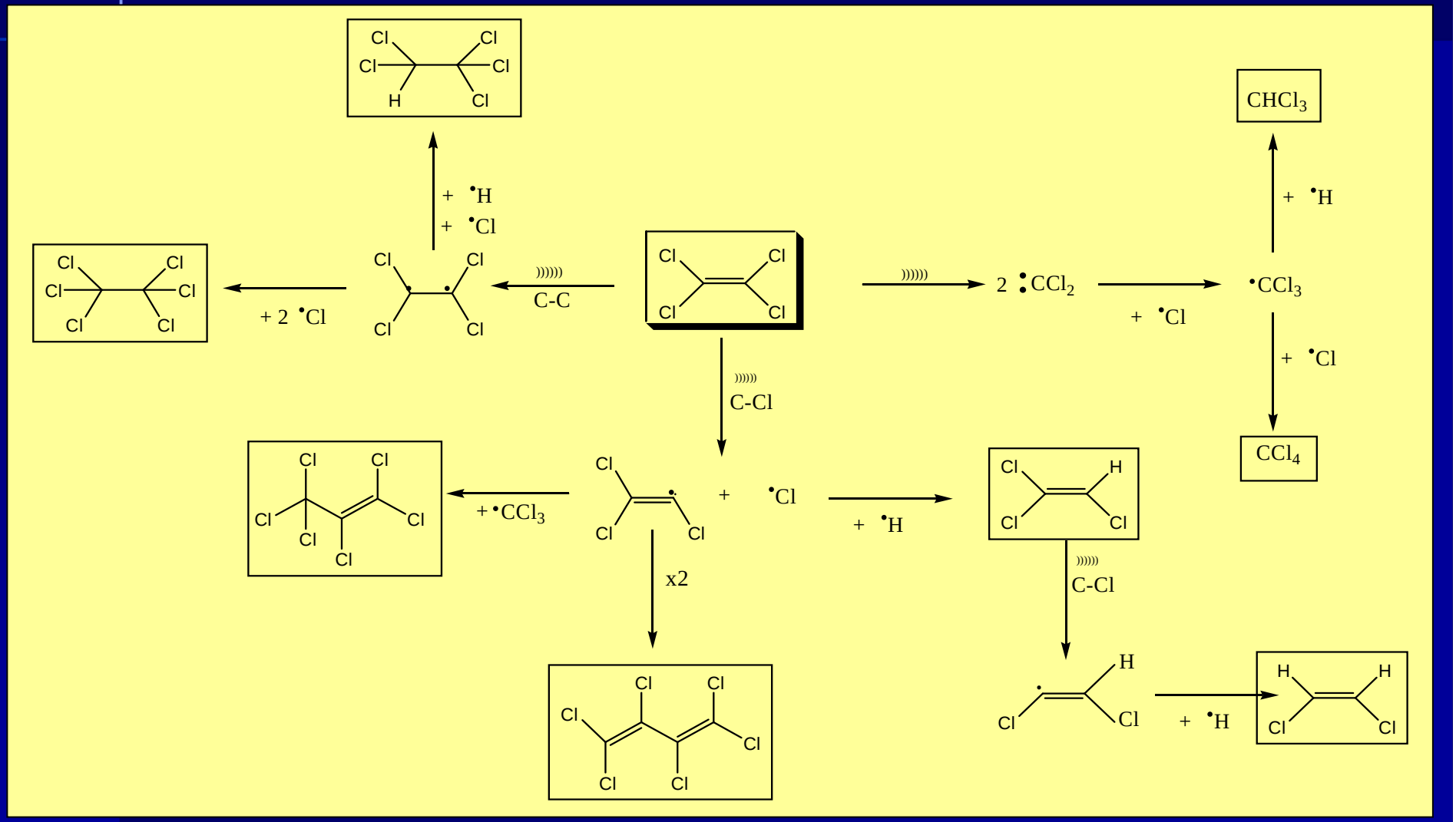
Mechanism:



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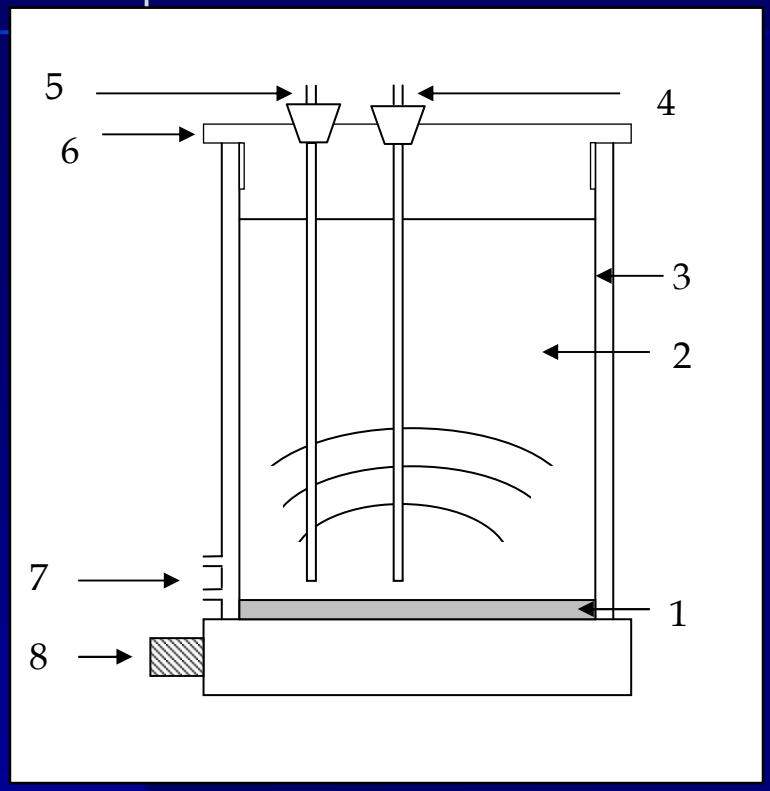
Experimental set-up



Sonoreactor Meinhardt Ultraschalltechnik, K80-5
Frequency: 850kHz
Maximum power output: 140W
Sonicated volume: 200cm^3

1) Transducer, 2) bulk solution, 3) glass cell, 4) sample withdrawing system, 5) temperature probe, 6) lid, 7) inlet and outlet of the cooling jacket and 8) interface

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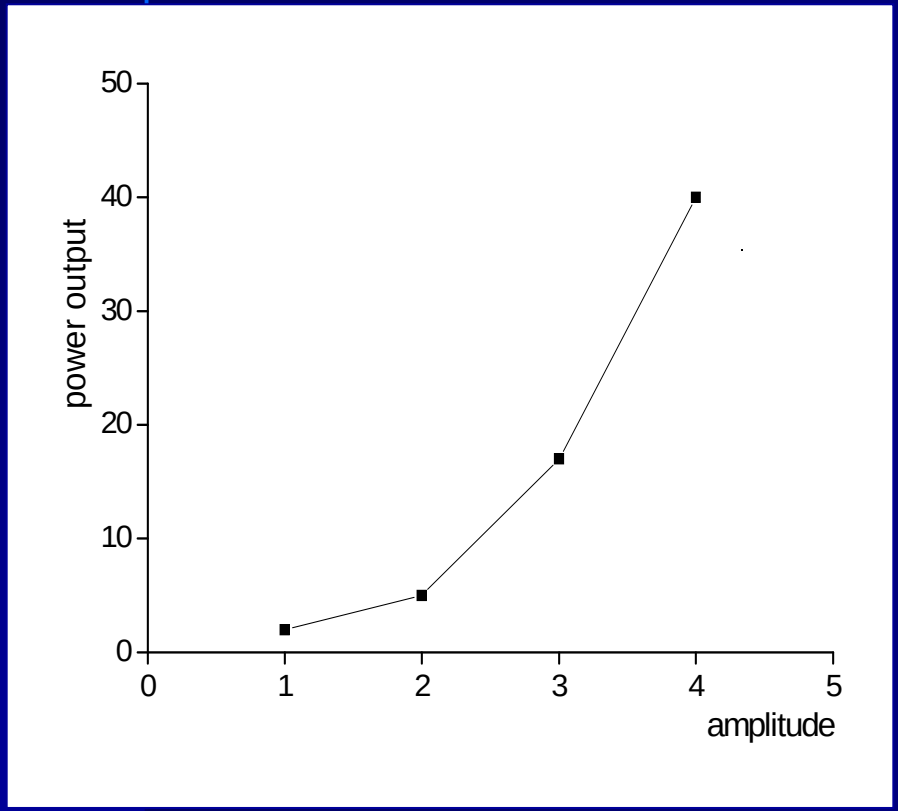
Characterization of the sonoreactor, 850kHz, 140W

Ultrasonic power output was measured using standard calorimetric procedures



Power input/ watts	W cm^{-2}	W cm^{-3}
2.2±0.2	0.11	0.01
4.7±0.1	0.24	0.02
17.2±0.9	0.88	0.07
37.9±4.4	1.93	0.15

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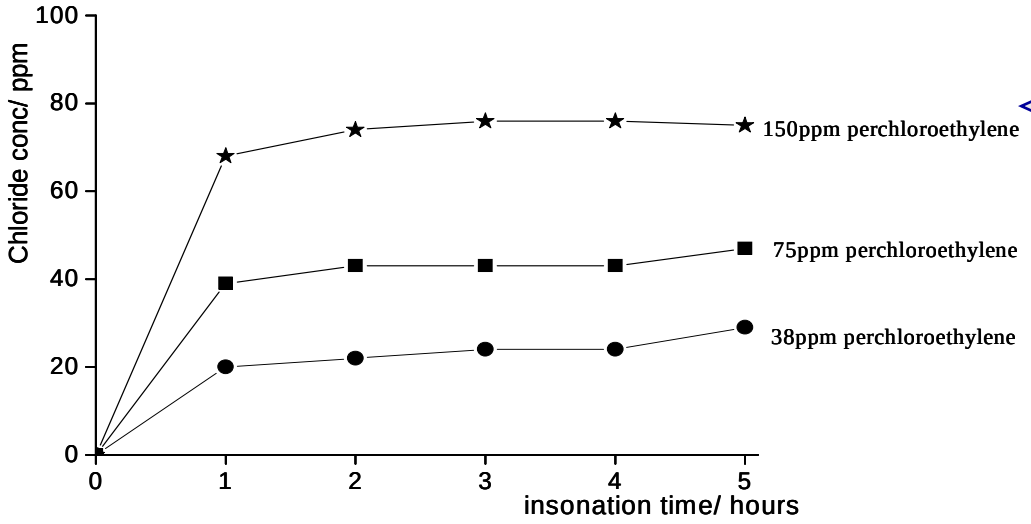
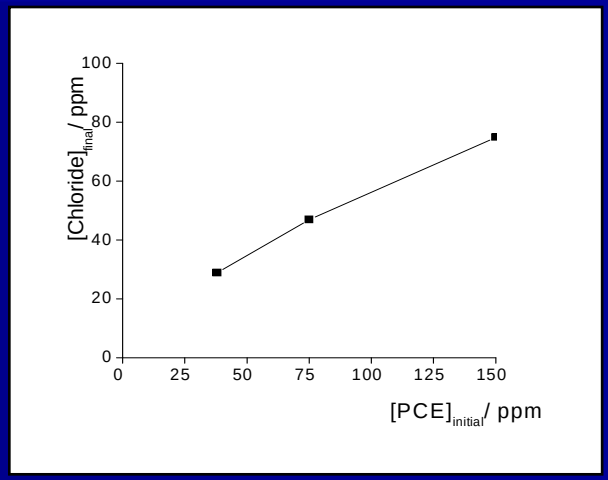
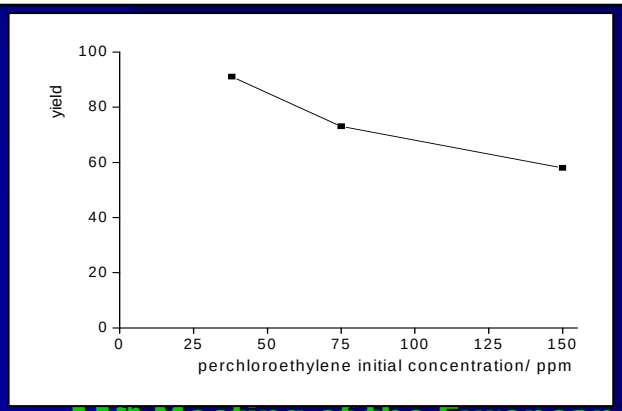
Effect of PCE concentration



150ppm PCE

Saturation conditions!!





Initial Perchloroethylene concentration/ ppm	*Yield of Cl^- formation/ %*
150	58
75	73
38	91

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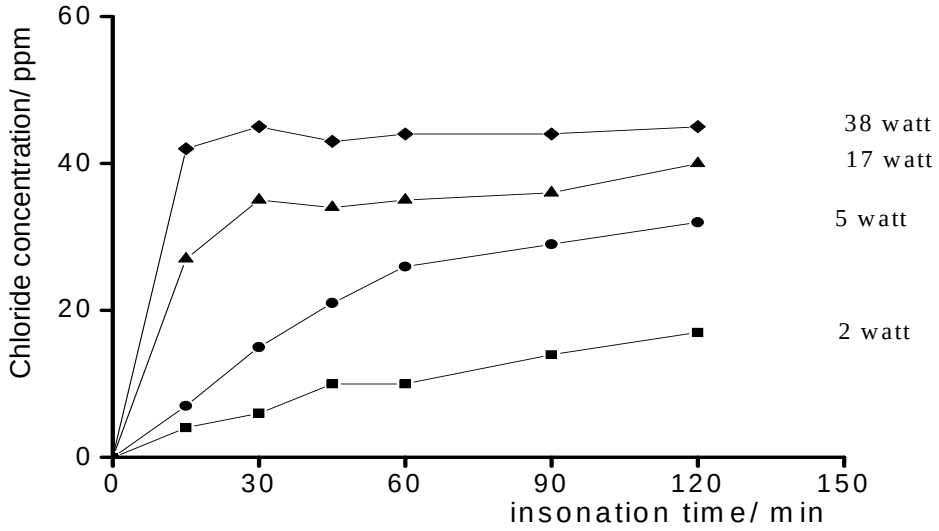
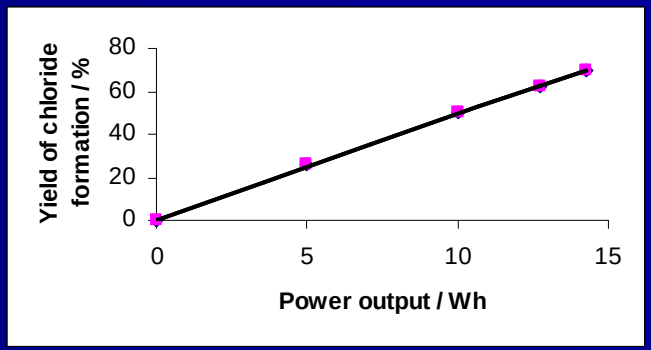
Effect of ultrasound power





Ultrasonic power / watts	*Yield of Cl^- formation/ %*
38	*70*
17	*62*
5	*50*
2	26

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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS RESULTS

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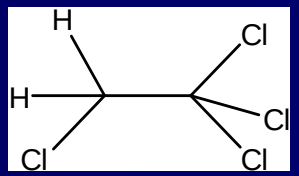
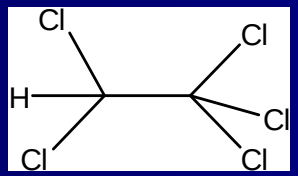
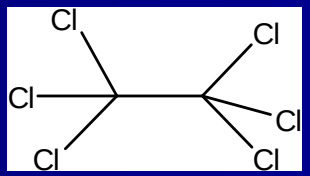
- Products from perchloroethylene sonochemical degradation at tracer level:

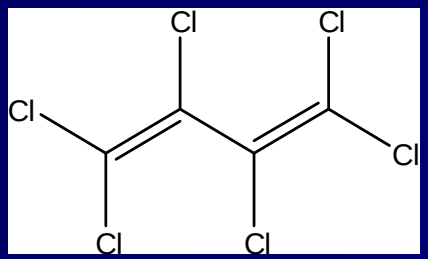
$CHCl_3$ CCl_4







Mechanism?



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SONOCHEMICAL DEGRADATION OF HALOCOMPOUNDS CONCLUSIONS

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- Perchloroethylene sonochemical degradation can be carried out
  - Different behaviour has been detected with the frequency
- Sonochemical degradation seems mainly to follow a pyrolytic radical mechanism
- Total degradation can not be stablished from the results coming from Cl^- detection
- Differences in the by-products obtained with different frequencies are still under study

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ACKNOWLEDGEMENTS

Coventry University
Generalidad Valenciana

Finantial Support
Alicante University
COST D32/004 (Electrochemistry with Ultrasound)

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Thank you!